2. THEORY OF PHOTOMETRIC MEASUREMENT

This section provides a brief review of the theory of photometric measurements, and then details how the SRP obtains and processes data in accordance with the photometric theory.

2.1 Physical Basis Of The Photometry Equation

Consider the transmission of light through a plane of area *A* that contains some number, *n*, of absorbing molecules. If radiation of intensity I_o is perpendicularly incident on the plane, and light of intensity I emerges from the plane, the transmittance, *T*, of the plane is defined as:

$$T = I/I_o$$

The transmittance is equal to:

1 - (fraction of light not transmitted)

or

1 - (area blocked by absorbing molecules)/(area of the plane, *A*)

The area blocked by the absorbing molecules is equal to the product of the area blocked by a single molecule times the number of molecules, and the equation for the transmittance can be written as:

$$T = 1 - (n x\sigma)/A \qquad \text{(Eq. 1)}$$

where σ is the effective absorption cross-sectional area of the absorbing species. The units of σ are cm^2/molecule; σ is a measure of the molecule's capacity to block light by absorbing it. It is often useful to consider σ to be a measure of the effective size of the molecule. The value of the effective absorption cross-sectional area depends on the following:

1. The nature of the absorbing species (*i.e.*, some species absorb light of a given wavelength, λ, while others do not).

2. The wavelength of the light (*i.e.*, the absorption of light by a molecule is different at different wavelengths). This property is what gives a species its characteristic spectrum. In terms of a simple model, this means that the effective size of a molecule is a function of the wavelength of light used to observe it.

3. The temperature and pressure of the gas when observing spectroscopic transitions in which both the upper and lower states are bound (*i.e.*, under conditions where the observed spectrum is a sharp line). Since the O_3 spectrum in the 250 nm wavelength region is primarily a broad continuum, the absorption cross-section is only slightly dependent on temperature and pressure. To within the accuracy required for measuring O_3 photometrically at 254 nm, one can assume that σ is a constant over ordinary temperatures and pressures.

If one considers a sample cell, such as the sample cell in a photometer, as having a finite length in addition to the area of the plane, Equation 1 can be rewritten as follows:

$$T = 1 - (n \times \sigma \times L)/(A \times L) = 1 - (n \times \sigma \times L)/V \qquad \text{(Eq. 2)}$$

where L is the length of the sample cell and V is the volume of the sample cell. The term n/V is a concentration in units of number density. The fact that the transmittance of a sample depends on the number density of the absorbing species is convenient because it allows one to correct photometric measurements for the temperature and pressure of the sample by simple gas law calculations.

Most chemists, air pollution technicians, and other workers making photometric measurements prefer to express concentration in units of atmospheres (a concentration of 1 atm equals the concentration of a gas at 1 atmosphere of pressure and standard temperature of 0^oC) and absorption coefficients in units of atm^{-1} cm^{-1} instead of molecules/cm^3 and cm^2/molecule, respectively. The ideal gas law can be written as follows:

Therefore, Equation 2 can be changed to atmospheres by multiplying the number density term by RT and dividing the absorption cross-section by the same factor. Letting:

And

Equation 2 becomes:

(Eq. 3)

This useful form of the photometry equation will be used later. First, consider the conditions for which the equation was derived. A basic assumption in the derivation is that the fraction of the light beam blocked by the absorbing molecules equals:

$$(n \times \sigma)/A$$

Or that the cross-sectional area of the beam that is blocked is n x σ. This assumption is valid only if the number of absorbing molecules in the sample is so small that one molecule never "shades" another. As soon as one molecule begins to shade another, the cross-sectional area of the beam that is blocked by these two molecules is less than 2 x σ.

To extend Equation 3 to the concentration and/or cell length range where significant shading of one molecule by others occurs (*i.e.*, the concentration range where one normally applies photometry), the length of the absorption volume is divided into small segments, dL, such that there is no shading within any small segment. The cumulative result is obtained by "adding" the intermediate result from each segment by mathematical integration.

Thus, Equation 3 can be rewritten as:

$$I_o - I = I_o \times (\alpha \times P \times L)$$

In integral form, this becomes:

$$*dI/I = -*(\alpha \times P \times dL)$$

or

$$\ln I = -(\alpha \times P \times L) + C$$

When P = 0, I = I_o, and C = ln I_o. The equation then becomes:

$$\ln (I/I_o) = -\alpha \times P \times L$$

or

$$T = (I/I_o) = e^{-\sigma PL} = 10^{-\sigma PL/2.30259} = 10^{-\sigma PL} \qquad \text{(Eq. 4)}$$

Equation 4 is the form of the photometry equation that is probably most familiar to the majority of air pollution measurement personnel. It is valid over wide concentration and cell length ranges. Equation 4 is usually known as the Bouguer-Lambert-Beer law or the Lambert-Beer law. The absorption coefficient, α, is called the absorptivity and is usually written simply as α when working in base 10. The concentration is normally designated by the letter c, and in most common usage, Equation 4 is written as follows:

$$T = (I/I_o) = 10^{-\alpha cL} = e^{-2.30259\alpha cL} \qquad \text{(Eq. 5)}$$

Note that Equation 5 contains five terms (I, I_o, α, c, and L), all of which can be measured. Furthermore, it is the ratio of I to I_o that is important rather than the absolute values of those quantities.

Frequently the Lambert-Beer law is written in logarithmic form with the term absorbance, A, often used to represent - log T:

$$A = - \log T = \alpha c L$$

When the absorbance (*i.e.*, the difference between I and I_o) is very small (as is typically the case when measuring the absorbance of sub-ppm_v levels of O_3), the Lambert-Beer law can be approximated in a linear form:

$$T = (I/I_o) = e^{-\alpha c L} \approx 1 - \alpha c L$$

since $e^{-x} \approx 1 - x$ for $x << 1$. Note that this approximation is identical to Equation 3. The error introduced by this approximation is not significant for O_3 concentrations smaller than ≈ 2 ppm_v (assuming a path length of less than 1 m), as will be shown below.

2.2 Sources Of Error In The Photometry Principle

The relative error in the concentration measurement is related to the relative error in the determinations of α, L, and T by the following equations:

$$(dc/c) = - (d\alpha/\alpha) \text{ (assuming no error in L or T)}$$
$$(dc/c) = - (dL/L) \text{ (assuming no error in α or T)}$$
$$(dc/c) = (dT/T\ln T) \text{ (assuming no error in α or L)}$$

The total error is the sum of these contributions.

The length of the optical path through the sample can normally be measured in a straightforward manner. The relative error associated with L should not exceed 1 mm; this corresponds to an error of approximately 0.1%. The absorption coefficient for a given species is measured in separate experiments and is normally available in the literature. Several investigators have determined absorption coefficient for O_3 at 254 nm under several different methods (see Table 2-1).[1]

[1] STANDARD OPERATING PROCEDURES AND RECERTIFICATION PROCEDURES FOR EPA'S STANDARD REFERENCE OZONE PHOTOMETER, EPA Contract 68-D3-0029, September 1997, TRC Environmental Corporation and National Institute of Standards and Technology (NIST)

The Absorption Coefficient has historically been based on a review of the literature (Hampson, 1973) using the value of α at 308±4 atm^{-1} cm^{-1} (base e) at standard temperature and pressure (STP) (273 K and 760 torr). BIPM is researching more up to date methods to be able to more accurately determine this value.

TABLE 2-l. OZONE ABSORPTION COEFFICIENT

Investigator(s), Year	**α (atm^{-1} cm^{-1}, base e)**	**Method**
Inn and Tanaka, 1953	306.2	Manometry
Griggs, 1968	303.9	Manometry
Becker et al., 1974	310.8	Manometry
Hearn, 1961	308.5	Decomposition Stoichiometry
DeMore and Raper, 1964	310.8	Decomposition Stoichiometry
Clyne and Coxon, 1968	312.2 (250 nm)	Gas Phase Titration

To make the transmittance measurement, the absorption cell is filled with a reference gas (zero air in the case of O_3), and the intensity of the light passing through the cell is recorded as I_o. The absorption cell is then filled with the sample, and the intensity of the light passing through the cell is recorded as I.

The error in the measurement of T is multiplied by the term 1/lnT. For a typical value of T of 0.99385 (0.2 ppm_v O_3; 100 cm path), this term is 160. Thus, the transmittance measurement must be accurate to 1 part in 16,000 to obtain a concentration accurate to 1 percent under the given conditions. Depending on choice of hardware, the transmittance measurement can be made with an accuracy of 1 part in 10^5 or better.

2.3 Photometric Measurements For Ozone

In order to understand how the SRP obtains the necessary data required in the determination of the O_3 concentration consider the following schematic pathways:

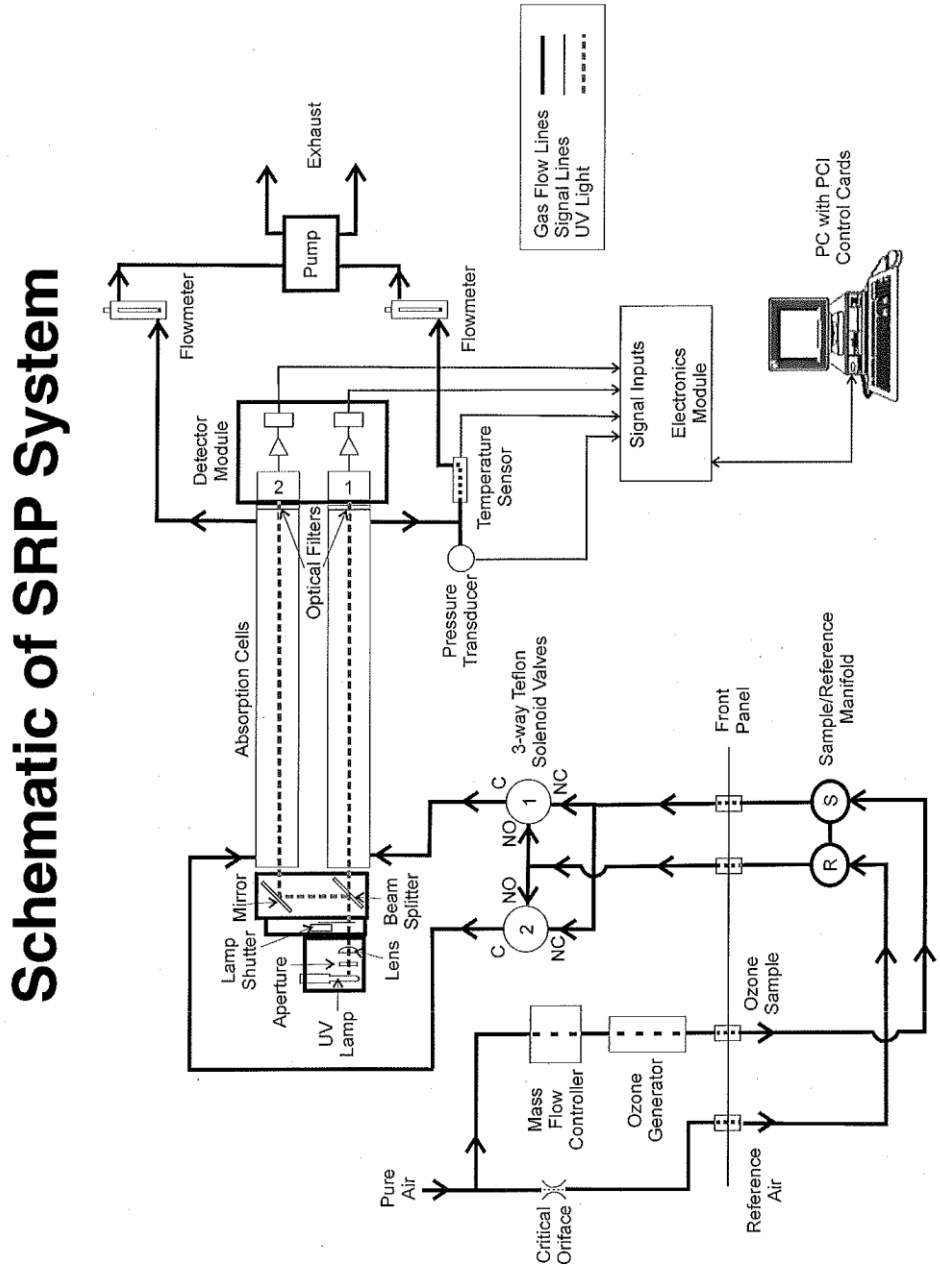

Figure 2-1. Simplified Schematic of the Standard Reference Photometer.

The O_3 concentration, c, is calculated from the expression:

T is the transmittance of the sample while the terms α (absorption coefficient) and L (path-length) are fixed quantities with known uncertainties. The commonly accepted value of α, 1.147 x 10^{-17} cm^2/molecule (or equivalently 308.32 atm^{-1} cm^{-1}, base e) (3), is expressed at STP. The sample temperature and pressure are measured, and the sample concentration is corrected using the ideal gas law.

A simplified schematic diagram of the SRP is given in Figure 2-1 showing the four frequencies (detector 1, detector 2, temperature, and pressure) produced during each cycle of the measurement process. These frequencies are integrated over five second periods by counting the total number of digital pulses with counter circuitry. To determine the transmittance of the sample with high precision, the SRP is programmed to alternately flow the sample through one cell and reference air through the second cell, and then flow the sample through the second cell and reference air through the first cell.

The terms L and α have been measured and are known to sufficient accuracy. Since the value of α has been reduced to STP, we need to measure the temperature and pressure so that the sample concentration can be corrected to actual measurement conditions. The SRP converts all four quantities to be measured (I, I_o, temperature, and pressure) to frequencies that are integrated for five-second periods by counting the total numbers of digital pulses with counter circuitry. In order to determine the transmittance of the sample with high precision, the instrument alternately (1) flows the sample through one cell and zero air through the second cell, and (2) flows the sample through the second cell and zero air through the first cell.

$$f_{1'} = K' f_{1nom} \text{ x } T_{cell(1)}$$

$$f_{2'} = K' f_{2nom}$$

The frequencies obtained during the first half-cycle of the instrument are:

where $f_{1'}$ and $f_{2'}$ are average (nominal) frequencies, K' is a factor which represents fluctuations in lamp intensity, and $T_{cell(1)}$ is the transmittance of cell 1. Similarly, during the second half-cycle, the frequencies are:

$$f_{1''} = K'' f_{1nom}$$

$$f_{2''} = K'' f_{2nom} \times T_{cell(2)}$$

If one defines ratios $R_1 = f_{1'} / f_{2'}$ and $R_2 = f_{1''} / f_{2''}$ and then takes the ratio of the data from the two half-cycles, one gets:

$$\frac{\quad}{\quad} = \frac{\quad}{\quad}$$

Upon cancelling like terms:

$$R = T_{cell(1)} \times T_{cell(2)}$$

which is the transmittance of a sample cell of length equal to that of cell 1 plus cell 2.

The SRP calculates the ratio R from the frequencies $f_{1'}$, $f_{1''}$, $f_{2'}$, and $f_{2''}$. It then computes the concentration from the equation:

$$c = \frac{-\ln(R)}{\sigma L}$$

Where c is the concentration in atmospheres, α is the O_3 absorption coefficient at 254 nm (308.32 atm^{-1} cm^{-1}, base e), and L is the cell path-length (89.65 cm). The SRP then applies a temperature/pressure correction factor:

$$F = \frac{Temp}{273.15} X \frac{1013.25}{Pressure}$$

This adjusts the concentration to take into account that α was specified for STP conditions. Finally, the SRP converts the concentration units from atmospheres to ppb_V by multiplying by 109.

In order to speed up replicate measurements, the SRP retains the value of the last computed minor ratio (*i.e.*, R_1 or R_2) and uses this information plus the minor ratio from the next half-cycle of the instrument to compute a new concentration value. In this way, it is possible to obtain N values for the concentrations from (N + 1) instrument half-cycles. For a more detailed decription on how the SRP calculates the Ozone concentration see NIST 6963 “STANDARD REFERENCE PHOTOMETER FOR THE ASSAY OF OZONE IN CALIBRATION ATMOSPHERS”.